

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 846 756 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
10.06.1998 Bulletin 1998/24

(51) Int. Cl.⁶: **C11D 17/00**

(21) Application number: **96203473.2**

(22) Date of filing: **06.12.1996**

(84) Designated Contracting States:
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE**
Designated Extension States:
AL LT LV RO SI

(71) Applicant:
THE PROCTER & GAMBLE COMPANY
Cincinnati, Ohio 45202 (US)

(72) Inventors:
• **Salager, Serge**
Merida 5101 (VE)

• **van Dijk, Paul Irma Albertus**
2580 Putte (BE)
• **van Poucke, Jeroen**
9160 Lokeren (BE)

(74) Representative:
Mather, Peter Geoffrey et al
Procter & Gamble
European Technical Center N.V.
Temselaan 100
1853 Strombeek-Bever (BE)

(54) **Coated detergent tablet**

(57) The present invention relates to tablets comprising a core and a coating, the core being formed by compressing a particulate material, the particulate material comprising surfactant and detergent builder, and the tablet further comprises a disintegrant, at least some of the disintegrant being in the coating.

The invention also relates to processes for making the tablets.

EP 0 846 756 A1

Description

The present invention relates to coated detergent tablets, especially those adapted for use in washing machines, and to processes for making the coated detergent tablets.

Although cleaning compositions in tablet form have often been proposed, these have not (with the exception of soap bars for personal washing) gained any substantial success, despite the several advantages of products in a unit dispensing form. One of the reasons for this may be that detergent tablets require a relatively complex manufacturing process. In particular, it is often desirable to provide the tablet with a coating and this adds to the difficulties of manufacture.

While tablets without a coating are entirely effective in use, they usually lack the necessary surface hardness to withstand the abrasion that is a part of normal manufacture, packaging and handling. The result is that uncoated tablets suffer from abrasion during these processes, resulting in chipped tablets and loss of active material.

Finally, coating of tablets is often desired for aesthetic reasons, to improve the outer appearance of the tablet or to achieve some particular aesthetic effect.

Numerous methods of tablet coating have been proposed, and many of these have been suggested for detergent tablets. However, all of these methods have certain disadvantages, as will be explained below.

GB-A-0 989 683, published on 22nd April 1965, discloses a process for preparing a particulate detergent from surfactants and inorganic salts; spraying on water-soluble silicate; and pressing the detergent particles into a solid form-retaining tablet. Finally a readily water-soluble organic film-forming polymer (for example, polyvinyl alcohol) provides a coating to make the detergent tablet resistant to abrasion and accidental breakage.

EP-A-0 002 293, published on 13th June 1979, discloses a tablet coating comprising hydrated salt such as acetate, metaborate, orthophosphate, tartrate, and sulphate.

EP-A-0 716 144, published on 12th June 1996, also discloses laundry detergent tablets with water-soluble coatings which may be organic polymers including acrylic/maleic co-polymer, polyethylene glycol, PVPVA, and sugar.

WO9518215, published on 6th July 1995, provides water-insoluble coatings for solid cast tablets. The tablets are provided with hydrophobic coatings including wax, fatty acid, fatty acid amides, and polyethylene glycol.

A disadvantage of the prior art disclosures is that a coating which is thick enough and strong enough to withstand abrasion, also tends to be slow to break up or dissolve in use.

The present invention provides a means by which tablets with a core which is formed by compressing a particulate material, the particulate material comprising surfactant and detergent builder, can be provided with a hard, thin, coating so that they can be stored, shipped and handled, but the coating is broken when the tablet is in the washing machine exposing the soft core which breaks up easily and rapidly, releasing the active ingredients into the wash solution.

The objective of the present invention is to provide a tablet which completely disintegrates and disperses, in particular in alkaline or surfactant-rich solutions such as the wash liquor.

Summary of the Invention

The object of the present invention is achieved by providing a tablet which further comprises a disintegrant, at least some of the disintegrant being in the coating. It is preferred that the tablet further comprises an effervescent, for example a soluble acid source and an alkali metal carbonate.

In a further aspect of the invention there is provided a process for making a tablet comprising the steps of :

(a) forming a core by compressing a particulate material, the particulate material comprising surfactant and detergent builder;

(b) applying a coating material to the core, the coating material being in the form of a melt;

(c) allowing the molten coating material to solidify; wherein the coating material comprises a disintegrant.

Preferably the coating materials have a melting point in the range of from 40 °C to 200 °C.

In an alternative to this embodiment of the invention there is provided a process for making a tablet comprising the steps of :

(a) forming a core by compressing a particulate material, the particulate material comprising surfactant and detergent builder;

(b) applying a coating material to the core, the coating material being dissolved in a solvent;

(c) allowing the solvent to evaporate; wherein the coating material comprises a disintegrant.

Detailed Description of the Invention

Tablets to be coated in the present invention can be prepared simply by mixing the solid ingredients together and compressing the mixture in a conventional tablet press as used, for example, in the pharmaceutical industry. Any liquid ingredients, for example the surfactant or suds suppressor, can be incorporated in a conventional manner into the solid particulate ingredients. Preferably the principal ingredients, are used in particulate form.

In particular for laundry tablets, the ingredients such as builder and surfactant can be spray-dried in a conventional manner and then compacted at a suitable pressure.

The detergent tablets can be made in any size or shape and can, if desired, be surface treated before coating, according to the present invention. In the core of the tablet is included a surfactant and a builder which normally provides a substantial part of the cleaning power of the tablet. The term "builder" is intended to mean all materials which tend to remove calcium ion from solution, either by ion exchange, complexation, sequestration or precipitation.

The particulate material used for making the tablet of this invention can be made by any particulation or granulation process. An example of such a process is spray drying (in a co-current or counter current spray drying tower) which typically gives low bulk densities 600g/l or lower. Particulate materials of higher density can be prepared by granulation and densification in a high shear batch mixer/granulator or by a continuous granulation and densification process (e.g. using Lodige® CB and/or Lodige® KM mixers). Other suitable processes include fluid bed processes, compaction processes (e.g. roll compaction), extrusion, as well as any particulate material made by any chemical process like flocculation, crystallisation sintering, etc. Individual particles can also be any other particle, granule, sphere or grain.

The particulate materials may be mixed together by any conventional means. Batch is suitable in, for example, a concrete mixer, Nauta mixer, ribbon mixer or any other. Alternatively the mixing process may be carried out continuously by metering each component by weight on to a moving belt, and blending them in one or more drum(s) or mixer(s). A liquid spray-on to the mix of particulate materials (e.g. non-ionic surfactants) may be carried out. Other liquid ingredients may also be sprayed on to the mix of particulate materials either separately or premixed. For example perfume and slurries of optical brighteners may be sprayed. A finely divided flow aid (dusting agent such as zeolites, carbonates, silicas) can be added to the particulate materials after spraying the non-ionic, preferably towards the end of the process, to make the mix less sticky.

The tablets may be manufactured by using any compacting process, such as tableting, briquetting, or extrusion, preferably tableting. Suitable equipment includes a standard single stroke or a rotary press (such as Courtoy®, Korch®, Manesty®, or Bonals®). The tablets prepared according to this invention preferably have a diameter of between 40mm and 50mm, and a weight between 25 and 60 g. The compaction pressure used for preparing these tablets need not exceed 5000 kN/m², preferably not exceed 3000 kN/m², and most preferably not exceed 1000 kN/m².

According to the present invention, the tablets are then coated with a coating so that the tablet does not absorb moisture, or absorbs moisture at only a very slow rate. The coating is also strong so that moderate mechanical shocks to which the tablets are subjected during handling, packing and shipping result in no more than very low levels of breakage or attrition. Finally the coating is preferably brittle so that the tablet breaks up when subjected to stronger mechanical shock. Furthermore it is advantageous if the coating material is dissolved under alkaline conditions, or is readily emulsified by surfactants. This avoids the deposition of undissolved particles or lumps of coating material on the laundry load. This may be important when the coating material is completely insoluble (for example less than 1 g/l) in water.

As defined herein "substantially insoluble" means having a very low solubility in water. This should be understood to mean having a solubility in water at 25°C of less than 20 g/L, preferably less than 5 g/l, and more preferably less than 1 g/l. Water solubility is measured following the test protocol of ASTM E1148-87 entitled, "Standard Test Method for Measurements of Aqueous Solubility".

Suitable coating materials are fatty acids, C2-C13 dicarboxylic acids, fatty alcohols, diols, esters and ethers. Preferred fatty acids are those having a carbon chain length of from C12 to C22 and most preferably from C18 to C22. Preferred dicarboxylic acids are oxalic acid (C2), malonic acid (C3), succinic acid (C4), glutaric acid (C5), adipic acid (C6), pimelic acid (C7), suberic acid (C8), azelaic acid (C9), sebacic acid (C10), undecanedioic acid (C11), dodecanedioic acid (C12) and tridecanedioic acid (C13). Preferred fatty alcohols are those having a carbon chain length of from C12 to C22 and most preferably from C14 to C18. Preferred diols are 1,2-octadecanediol and 1,2-hexadecanediol. Preferred esters are tristearin, tripalmitin, methylbehenate, ethylstearate. Preferred ethers are diethyleneglycol mono hexadecylether, diethyleneglycol mono octadecylether, diethyleneglycol mono tetradecylether, phenylether, ethyl naphtyl ether, 2 methoxynaphtalene, beta naphtyl methyl ether and glycerol mono octadecylether. Other preferred coating materials include dimethyl 2,2 propanol, 2 hexadecanol, 2 octadecanone, 2 hexadecanone, 2, 15 hexadecanedione and 2 hydroxybenzyl alcohol.

However the detergent tablets are prepared and in whatever form they are, they are then coated according to the present invention with a coating material having a melting point preferably of from 40 °C to 200 °C.

The coating can be applied in a number of ways. Two preferred coating methods are a) coating with a molten material and b) coating with a solution of the material.

In a), the coating material is applied at a temperature above its melting point, and solidifies on the tablet. In b), the coating is applied as a solution, the solvent being dried to leave a coherent coating. The substantially insoluble material can be applied to the tablet by, for example, spraying or dipping. Normally when the molten material is sprayed on to the tablet, it will rapidly solidify to form a coherent coating. When tablets are dipped into the molten material and then removed, the rapid cooling again causes rapid solidification of the coating material. Clearly substantially insoluble materials having a melting point below 40 °C are not sufficiently solid at ambient temperatures and it has been found that materials having a melting point above about 200 °C are not practicable to use. Preferably, the materials melt in the range from 60 °C to 160 °C, more preferably from 70 °C to 120 °C.

By "melting point" is meant the temperature at which the material when heated slowly in, for example, a capillary tube becomes a clear liquid.

A coating of any desired thickness can be applied according to the present invention. For most purposes, the coating forms from 1% to 10%, preferably from 1.5% to 5%, of the tablet weight.

The tablet coatings of the present invention are very hard and provide extra strength to the tablet.

In the present invention the fracture of the coating in the wash is improved by adding a disintegrant in the coating.

This disintegrant will swell once in contact with water and break the coating in small pieces. This will improve the dissolution of the coating in the wash solution. The disintegrant is suspended in the coating melt at a level of up to 30%, preferably between 5 and 20%, and most preferably between 5 and 10% by weight.

Possible disintegrants are described in Handbook of Pharmaceutical Excipients (1986). Examples of suitable disintegrants include starch: natural, modified or pregelatinized starch, sodium starch gluconate; gum: agar gum, guar gum, locust bean gum, karaya gum, pectin gum, tragacanth gum; croscarmellose Sodium, croscopovidone, cellulose, carboxymethyl cellulose, alginic acid and its salts including sodium alginate, silicone dioxide, clay, polyvinylpyrrolidone, soy polysaccharides, ion exchange resins and mixtures thereof.

Depending on the composition of the starting material, and the shape of the tablets, the used compaction force will be adjusted to not affect the strength (Diametral Fracture Stress), and the disintegration time in the washing machine.

This process may be used to prepare homogenous or layered tablets of any size or shape.

Diametral Fracture Stress (DFS) is a way to express the strength of a tablet, it is determined by the following equation :

$$= \frac{2 F}{\mu D t}$$

Where F is the maximum force (Newton) to cause tensile failure

(fracture) measured by a VK 200 tablet hardness tester supplied by Van Kell industries, Inc. D is the diameter of the tablet, and t the thickness of the tablet. (Method Pharmaceutical Dosage Forms : Tablets Volume 2 Page 213 to 217)

The rate of disintegration of a detergent tablet can be determined in two ways :

a) In a "VAN KEL" Friabilator with "Vankel Type" drums.

- Put 2 tablets with a known weight and D.F.S in the Friabilator drum.
- Rotate the drum for 20 rotations.
- Collect all product and remaining tablet pieces from the Friabilator drum, and screen it on 5 mm, and through 1.7 mm
- Express as % residue on 5 mm and through 1.7 mm.
- The higher the % of material through 1.7 mm the better the disintegration.

b) In a washing machine according to the following method

- Take two tablets with a known weight and fracture stress, and put them at the bottom of a washing machine (i.e. a Bauknecht WA 950).
- Put a 3 kg mixed load on top of the tablets.
- Run a 30 °C short cycle (program 4) with city water.
- Stop the cycle after 5 min and check the wash load for undissolved tablet pieces, collect and weigh them, and record the percent residue left.

In another preferred embodiment of the present invention the tablets further comprises an effervescent. Effervescency as defined herein means the evolution of bubbles of gas from a liquid, as the result of a chemical reaction

between a soluble acid source and an alkali metal carbonate, to produce carbon dioxide gas, i.e.



- 5 Further examples of acid and carbonate sources and other effervescent systems may be found in : (Pharmaceutical Dosage Forms : Tablets Volume 1 Page 287 to 291)

An effervescent may be added to the tablet mix in addition to the detergent ingredients. The addition of this effervescent to the detergent tablet improves the disintegration time of the tablet. The amount will preferably be between 5 and 20 % and most preferably between 10 and 20% by weight of the tablet. Preferably the effervescent should be added as an
10 agglomerate of the different particles or as a compact, and not as separated particles.
Due to the gas created by the effervescency in the tablet, the tablet can have a higher D.F.S. and still have the same disintegration time as a tablet without effervescency. When the D.F.S. of the tablet with effervescency is kept the same as a tablet without, the disintegration of the tablet with effervescency will be faster.

15 Detergent surfactants

Nonlimiting examples of surfactants useful herein typically at levels from about 1% to about 55%, by weight, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃M⁺) CH₃ and CH₃(CH₂)_y(CHOSO₃M⁺) CH₂CH₃ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AES"), especially EO 1-7 ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-C₁₈ glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxy
25 alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like, can also be included in the overall compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional
30 soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

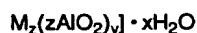
Builders

35 Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils. The level of builder can vary widely depending upon the end use of the composition. Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the triphosphates, pyrophosphates, and glassy polymeric metaphosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulfates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate
45 builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO₂:Na₂O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na₂SiO₅ morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula NaMSi_xO_{2x+1} · yH₂O wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na₂SiO₅ (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.
55 Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Appli-

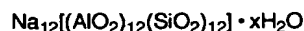
cation No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof. Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity.

Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium

pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

5 Bleach

The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric
10 laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator. The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate)
15 can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984,
20 U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxydecanoic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al. Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by
25 DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers.
30 Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854,
35 issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

Highly preferred amido-derived bleach activators are those of the formulae:



wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and
45 L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate, and mixtures thereof as
50 described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:

55